possible to make wholly reliable assessments of the limits of error; the values given are only somewhat rough estimates.

PASADENA 4, CALIF. RECEIVED MARCH 9, 1950

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Electrolytic Properties of Aqueous Solutions of Polyacrylic Acid and Sodium Hydroxide. II. Diffusion Experiments Using Radioactive Sodium[1]

BY JOHN R. HUIZENGA,[2] PHILIP F. GRIEGER AND FREDERICK T. WALL

I. Introduction

Previous work[3] on the electrical transference properties of polyacrylic acid–sodium hydroxide solutions, using radioactive sodium as a tracer, has shown that a significant fraction of the sodium ions are associated with the polymer. Kern[4] arrived at a similar conclusion, but his estimates of the fraction of associated sodium, based on osmotic pressure and conductance measurements, are in poor agreement with each other as well as with our transference results. In making his computations from conductance measurements, Kern assumed that a negligible fraction of the current was carried by polymer ion. Transference measurements, however, show this assumption to be invalid, for over the range 25 to 100% neutralization, the polymer ion carries roughly half the current. Consequently, Kern's estimate based on conductivities gives much too low a value for bound sodium. On the other hand, his osmotic pressure measurements appear to lead to values which are too high, judging from his observed osmotic pressures for pure acid solution, which are as much as 30% lower than those computed from the *p*H values of the solutions.

Our results obtained from transference experiments are roughly midway between Kern's two estimates, but in view of the poor agreement between the three methods, it appeared worthwhile to test the validity of the transference results in another way. This report gives the results of such a test, made by measuring the diffusion of radioactive sodium in otherwise uniform solutions of polyacrylic acid and sodium hydroxide, using the steady state technique.[5,6] The present work confirms the transference results.

II. Basis of the Experiments

Radioactive tracers are particularly suitable for diffusion experiments because they can be used to follow molecular or ionic movements in systems of uniform total concentration. Consider a solution of an electrolyte, $C_{\nu_1}A_{\nu_2}$, with its corresponding tracer, $C^*_{\nu_1}A_{\nu_2}$, and let the cation charge be e_1 and the anion charge e_2. Let us denote the concentrations of the ions of C, C* and A by n_1, n_1^* and n_2, respectively. Then in one dimension, the flow equations are[7]

$$J_1 = -kT\,\omega_1\,\partial n_1/\partial x - kTn_1\omega_1\,\partial \ln \gamma_1/\partial x + n_1\,\omega_1 e_1 E$$
$$J_1^* = -kT\,\omega_1\,\partial n_1^*/\partial x - kTn_1^*\omega_1\,\partial \ln \gamma_1/\partial x + n_1^*\,\omega_1 e_1 E$$
$$J_2 = -kT\,\omega_2\,\partial n_2/\partial x - kTn_2\omega_2\,\partial \ln \gamma_2/\partial x + n_2\,\omega_2 e_2 E$$

where k is Boltzmann's constant, γ_i the appropriate activity coefficient, E the electric field intensity and ω_i the mobility of the i^{th} species.

Let us now imagine a diffusion cell consisting of two compartments, only one of which originally contains tracer. In particular, if n_2 is constant throughout the cell, it is clear that in the absence of an external field, $E = 0$, $\partial \ln \gamma_i/\partial x = 0$, $J_2 = 0$ and $\partial n_1/\partial x + \partial n_1^*/\partial x = 0$. Then

$$J_1^* = -kT\omega_1 \partial n_1^*/\partial x$$

so a measurement of the tracer flow will enable one to calculate the corresponding ionic mobility providing the concentration gradient of tracer is known. For this particular system, the diffusion coefficient should be defined as

$$D_1^* = kT\omega_1 \qquad (1)$$

Clearly D_1^* does not depend upon either ω_2 or the activity coefficients.

Now let us consider a slightly different system in which n_1 is initially uniform throughout the diffusion cell. If tracer is now added to one of the compartments, then n_2, as well as n_1^*, will not be the same on both sides. Under these circumstances, E and $\partial \ln \gamma_i/\partial x$ are not exactly zero, although they can be estimated as follows. To compute the order of magnitude of E, first neglect the activity coefficient terms. Then if we stipulate zero electric current, $e_1J_1 + e_1J_1^* + e_2J_2 = 0$, and electroneutrality, $n_1e_1 + n_1^*e_1 + n_2e_2 = 0$, it follows that

$$E = \frac{kT(\omega_2 - \omega_1)\,\partial n_2/\partial x}{(e_2\omega_2 - e_1\omega_1)n_2}$$

Putting the above expression for E into the flow equations discloses that the third term of J_1^* is less than the first term by a factor of the order of magnitude n_1^*/n_1 providing $|\partial n_1/\partial x|$ is not substantially greater than $|\partial n_1^*/\partial x|$, which is certainly true.

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] Argonne National Laboratories Chicago, Ill.

[3] Huizenga, Grieger and Wall, THIS JOURNAL, **72**, 2636 (1950).

[4] Kern, *Z. physik. Chem.*, **A181**, 249 (1937–1938); **A181**, 283 (1937–1938); **A184**, 197 (1939); **A184**, 302 (1939).

[5] Gordon, *Ann. N. Y. Acad. Sci.*, **46**, 285 (1945).

[6] Brady and Salle, THIS JOURNAL, **70**, 914 (1948).

[7] Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

To estimate the order of magnitude of the activity coefficient term, let us assume that

$$\ln \gamma_i = A_i\Gamma^{1/2}$$

where Γ, the ionic strength, is equal to $(n_1 + n_1^*)\cdot\nu_2(\nu_1 + \nu_2)$. Differentiating $\ln \gamma_i$ with respect to x, we find

$$\frac{\partial \ln \gamma_i}{\partial x} = \frac{\ln \gamma_i}{2(n_1 + n_1^*)}\left(\frac{\partial n_1}{\partial x} + \frac{\partial n_1^*}{\partial x}\right)$$

Substituting the above into the expression for J_1^* it is found that the second term is less than the first by a factor of the order of magnitude $n_1^*\ln\gamma_1/n_1$ which is also negligible. By similar arguments it is readily shown in general that if the only non-uniformities of total concentration are caused by the addition of relatively small amounts of tracer, the diffusion coefficient D_1^* should be taken as $kT\omega_1$ in accordance with equation (1). Although Onsager[8] has already indicated that the local electric field term as well as the activity coefficient term will be negligible in computing the tracer flow, there appears to be some confusion on this point.[9] It is worth noting, however, that the above conclusions regarding tracer flow are not necessarily true for the non-tracer species.

For polyacrylic acid–sodium hydroxide solutions, assume for the sake of simplicity that there is only one species of polymer ion present, with degree of polymerization, s, charge, i, and number of associated sodium ions, j. Also let ρ_{Na} and ρ_{p} be the ratio of radioactive to total sodium ions in the sodium ion and polymer ion species, and let n_{Na} and n_{p} be their concentrations. Also let

Λ_{p} and Λ_{Na} equal the equivalent conductances of polymer ion and sodium ion
c = stoichiometric concentration of polyacrylic acid (equiv./L)
r = stoichiometric concentration of sodium hydroxide (equiv./L)
f = fraction of sodium ions unassociated with polymer

Then if n_{Na} and n_{p} are uniform, the flow of radioactive sodium is

$$J^* = -kT(\omega_{\text{Na}}n_{\text{Na}}\partial\rho_{\text{Na}}/\partial x + j\omega_{\text{p}}n_{\text{p}}\partial\rho_{\text{p}}/\partial x).$$

Transference experiments[3] on the solutions in question indicate that the second term is small compared to the first. The validity of this statement is justified by a computation of

$$j\omega_{\text{p}}n_{\text{p}}/\omega_{\text{Na}}n_{\text{Na}} = (j/s)\Lambda_{\text{p}}c/(i/s)\Lambda_{\text{Na}}rfs$$

using the results of the transference measurements.[3] Since s is in the neighborhood of a thousand,[10] it turns out that flow of tracer in polymer ion is only 0.5% or less of the flow of tracer as free sodium ions. Accordingly it will be assumed that

$$J^* = -D_{\text{Na}}^*n_{\text{Na}}\partial\rho_{\text{Na}}/\partial x \qquad (2)$$

where the diffusion coefficient of tracer is defined by equation (1).

It was pointed out in connection with the transference experiments that the exchange of radioactive sodium between polymer ions and free sodium ions takes place at a finite rate.[3] This fact has a bearing on the procedure to be followed in transference experiments and the question arises as to whether or not a uniform gradient can be established in the "steady state" diffusion experiment. If the appropriate equations of continuity are[3]

$$-n_{\text{Na}}\partial\rho_{\text{Na}}/\partial t = \partial J_{\text{Na}}^*/\partial x + k(\rho_{\text{Na}} - \rho_{\text{p}}) \qquad (3)$$

$$-jn_{\text{p}}\partial\rho_{\text{p}}/\partial t = \partial J_{\text{p}}^*/\partial x - k(\rho_{\text{Na}} - \rho_{\text{p}}) \qquad (4)$$

where J_{Na}^* and J_p^* represent the flow of tracer in sodium ions and polymer ions, respectively, and the "k" terms account for the exchange effect, then the usual steady state result is obtained if $\partial J_{\text{p}}^*/\partial x$ can be neglected. In this event, it is seen by setting the time derivatives equal to zero that

$$\rho_{\text{p}} = \rho_{\text{Na}} = \rho$$

and

$$\partial J_{\text{Na}}^*/\partial x = -D_{\text{Na}}^*n_{\text{Na}}\partial^2\rho/\partial x^2 = 0 \qquad (5)$$

The diffusion cell consists of two end compartments "a" and "b" of volumes V_{a} and V_{b} separated by a frit of negligible volume, of effective cross section A and thickness L. The solutions in each end compartment are mixed perfectly, so that throughout compartment "a," for example

$$\rho_{\text{p}} = \rho_{\text{Na}} = \rho_{\text{a}}$$

At $t = 0$, let $\rho_{\text{a}} = \rho^\circ$, $\rho_{\text{b}} = 0$, $\partial\rho/\partial x = -\rho^\circ/L$. The variation in ρ_{a} and ρ_{b} with time is supposed to be small enough so that, for all t

$$\partial\rho/\partial x = -(1/L)(\rho_{\text{a}} - \rho_{\text{b}})$$

Let

$$R = \frac{\text{counts/min. cm.,}^3\text{ soln. side "b" at time} = t}{\text{counts/min. cm.,}^3\text{ soln. side "a" at time} = 0}$$

Integration of the appropriate equations under the stated initial and boundary conditions leads to the familiar expression

$$-fD_{\text{Na}}^*\,Kt = \log(1 - R(1 + V_{\text{b}}/V_{\text{a}})) \qquad (6)$$

where the customary definition of the cell constant, $K = (A/L)(V_{\text{a}} + V_{\text{b}})/2.303\,V_{\text{a}}V_{\text{b}}$, has been used. Since the exchange of tracer between polymer ion and sodium ion is probably finite, equation (6) is valid only if the flow of radioactive sodium in polymer ion is negligible. In writing equations (3) and (4), the existence of only one polymer species was assumed for simplicity. If these were generalized by considering a number of equations like (4) and including the sum of all the exchange terms in (3), then equations (5) and (6) could still hold, providing the flow of tracer in each of the species is zero. Diffusion experiments using tracer can then be regarded as giving a measure of the total free sodium ion concentration irrespective of the distribution of bound sodium ions in various possible polymeric species.

III. Experimental

Procedure.—All the experiments were done in duplicate, using two different cells. The approximate cell dimen-

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[8] Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945); see his eq. (56).

[9] Adamson, *J. Chem. Phys.*, **71**, 762 (1947).

[10] On the basis of unpublished light scattering measurements made in this Laboratory.

sions are: over-all length, 16 cm.; diameter, 3 cm.; V_a and V_b, 60 to 70 $cm.^3$; $V_b/V_a = 0.9864$ for cell 1, 0.9709 for cell 2; thickness of frit (Pyrex, fine), 2 mm. One-inch lengths of glass rod were put into each end compartment to serve as stirrers; the cells were rotated end-over-end at about 3 r.p.m.

The cells were filled as follows. First of all, two polyacrylic acid–sodium hydroxide solutions with the same stoichiometric concentrations were prepared volumetrically. One was made from ordinary sodium hydroxide, the other from sodium hydroxide containing Na^{22} as tracer.[11] End compartment "b" and the frit were filled with the non-radioactive solution and compartment "a" with the solution containing tracer. The cell was rotated for four hours after which the end compartments were refilled with the respective original solutions. The cells were again rotated for about two days. At the end of this time the radioactivity of compartment "b" was determined. As usual it was assumed that in the frit at the start of the second period of diffusion, $\partial\rho/\partial x = -\rho^\circ/L$. A negligible error is made in this way.

The diffusion apparatus was not thermostated. During the period of experimentation, the room temperature fluctuated very little from 25°. In any event the uncertainty in the results by reason of variations in temperature is only about one half that caused by the radioactivity counting error.

Materials and Radioactivity Counting Procedure.—The polyacrylic acid employed was identical with that used in the transference experiments[3] described previously. Likewise, the counting procedure for determining radioactivity was the same as that reported earlier.[3]

IV. Results

Sodium Chloride Solutions. Cell Constant Determination.—The accepted procedure for calibrating the diffusion cell in the steady state experiment involves a determination of the diffusion of 0.1 *N* potassium chloride in water.[5] This is an appropriate procedure when ordinary diffusion experiments are to be made in the cell. Since the mobilities of the ions are constant throughout the frit in the self-diffusion experiments, it appeared preferable to determine the cell constant by measuring the diffusion of tracer in solutions whose ion mobilities are known. For this reason the diffusion of radioactive sodium ion in sodium chloride solutions was determined. The work of Brady and Salley[6] as well as that of Adamson[9] indicates that this is a reasonable procedure, since their cell constants, determined by diffusion experiments involving a finite difference in concentration, appear to be too low by as much as 7 to 15%, judging from their self-diffusion results.

In Table I are given the results of experiments on the diffusion of radioactive sodium in sodium chloride solutions at four concentrations. The cell constant, *K*, was computed from equation (6) using the limiting relation, valid at infinite dilution

$$D^*_{Na} = kT\omega_{Na} = 0.02300\Lambda_{Na} \text{ (with } T = 298.1)$$

The values of Λ_{Na} were obtained graphically from conductance and transference data on sodium chloride solutions.[12] At the relatively high concentrations involved in Table I, the fact that the *K* values do not exhibit a trend indicates that this assumption is a reasonable one. The average *K* values, namely, 0.0357 $cm.^{-2}$ for cell 1 and 0.0378 $cm.^{-2}$ for cell 2, were used in connection with the polyacrylic acid–sodium hydroxide results. For the four determinations the mean deviations amounted to 2.5% for cell 1 and 0.8% for cell 2. Markedly lower values were obtained by the usual

TABLE I

SODIUM CHLORIDE SOLUTIONS: DETERMINATION OF CELL CONSTANTS

Cell	$10^2 \times$ sodium chloride concn., equiv./l.	$10^2 \times R$	t, days	D^*_{Na}, used	$10^2 \times K$, $cm.^{-2}$
1	0.200	8.094	1.879	1.112	3.64
2		8.449	1.881		3.78
1	0.400	8.115	2.007	1.097	3.47
2		8.817	2.009		3.76
1	1.00	7.991	1.903	1.068	3.69
2		8.353	1.905		3.84
1	2.00	7.491	1.930	1.039	3.49
2		8.078	1.932		3.75

TABLE II

THE QUANTITY fD^*_{Na} FOR POLYACRYLIC ACID-SODIUM HYDROXIDE SOLUTIONS

Cell	% Neutralization	$10^2 \times R$	t, days	fD^*_{Na}, sq. cm./day
		0.00378 *N* Polyacrylic Acid		
1	61.7	5.956	2.113	0.73
2		6.026	2.115	0.69
		0.0151 *N* Polyacrylic Acid		
1	9.60	7.969	2.012	1.04
2		8.317	2.015	1.02
1	24.0	6.462	1.874	0.89
2		6.707	1.877	.87
1	41.3	5.311	1.969	.69
2		5.517	1.971	.67
1	61.7	5.191	2.412	.55
2		5.838	2.413	.58
1	81.6	3.354	1.972	.43
2		3.598	1.975	.43
1	97.9	4.098	2.528	.41
2		4.431	2.530	.41
		0.0378 *N* Polyacrylic Acid		
1	9.60	7.667	2.057	.98
2		8.049	2.058	.96
1	24.0	5.559	1.894	.75
2		6.138	1.897	.78
1	41.3	6.293	2.591	.63
2		6.590	2.592	.62
1	61.7	4.957	2.405	.52
2		5.199	2.404	.52
1		4.604	2.305	.51
2		4.983	2.308	.52
1	81.6	4.348	2.449	.45
2		4.527	2.452	.44
1	97.9	4.201	2.688	.39
2		4.648	2.690	.41

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(11) The tracer was obtained from Prof. A. L. Hughes of Washington University, St. Louis, Missouri.

(12) Longsworth, THIS JOURNAL, **54**, 2741 (1932); Shedlovsky, Brown and MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1934).

method employing 0.1 N potassium chloride, namely. 0.0325 for cell 1 and 0.0347 for cell 2.

Polyacrylic Acid–Sodium Hydroxide Mixtures. —The product fD^*_{Na}, computed by means of equation (6), is listed in Table II as a function of per cent. neutralization = $100\ r/c$. The results are shown graphically in Figs. 1 and 2.

Two pairs of experiments are listed for 61.7% neutralization and c = 0.0378. The first pair of experiments was performed as described above. At the end of these experiments fresh solutions were placed in the end compartments, without disturbing the solution in the frit, and diffusion was allowed to proceed for another period of about two days. The end solutions were then analyzed as usual. The good agreement of the results indicates that the four-hour period allowed for the preliminary diffusion is long enough and that the error made by assuming $\partial\rho/\partial x = -\rho^\circ/L$ at the start of the actual diffusion period is not serious.

V. Discussion

On extrapolating the curves shown in Figs. 1 and 2 to zero neutralization, the following limiting values of fD^*_{Na} are obtained: 1.14 at c = 0.0151 N, and 1.14 at c = 0.0378 N. These values differ but slightly from the value of D^*_{Na} corresponding to $\Lambda^\circ_{\mathrm{Na}}$ = 50.1, which is 1.153. Even though the viscosities of the pure acid solutions are about three times that of water, it is evident that the mobility of sodium ion is not altered significantly by the presence of polyacrylic acid.[3]

The fraction of sodium ions associated with polymer, $1 - f$, is given in Table III. For convenience of comparison, the values obtained by transference measurements[3] are also included and the results compared graphically in Figs. 3 and 4. The estimates of Λ_{Na}, on which the values of D^*_{Na} are based, are the same as those used in connection with the transference experiments, and the method used in obtaining them has been described in the first paper of this series.[3]

TABLE III

FRACTION SODIUM IONS ASSOCIATED. COMPARISON OF DIFFUSION AND TRANSFERENCE[3] RESULTS

% Neutralization	Average fD^*_{Na}	Λ_{Na} used	D^*_{Na} used	Fraction sodium associated, $1 - f$ Diffusion	Transference[3]
		0.00378 N Polyacrylic Acid			
61.7	0.71	48.7	1.12	0.37	..
		0.0151 N Polyacrylic Acid			
9.60	1.03	48.7	1.12	0.080	0.10
24.0	0.88	48.1	1.11	.21	.27
41.3	.68	47.8	1.10	.38	.42
61.7	.56	47.7	1.10	.49	.55
81.6	.43	47.5	1.09	.61	.62
97.9	.41	47.3	1.09	.62	.62
		0.0378 N Polyacrylic Acid			
9.60	0.97	48.0	1.10	0.12	.14
24.0	.77	47.1	1.08	.29	.27
41.3	.63	46.6	1.07	.41	.41
61.7	.52	46.4	1.07	.51	.54
81.6	.44	46.1	1.06	.59	.60
97.9	.40	45.9	1.06	.62	.62

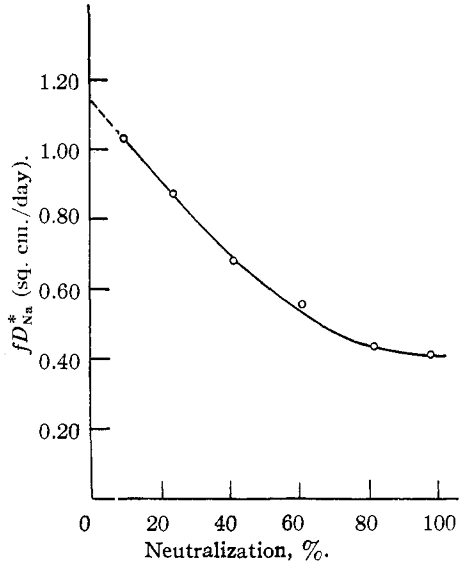

Fig. 1.—fD^*_{Na} as a function of neutralization for 0.0151 N polyacrylic acid.

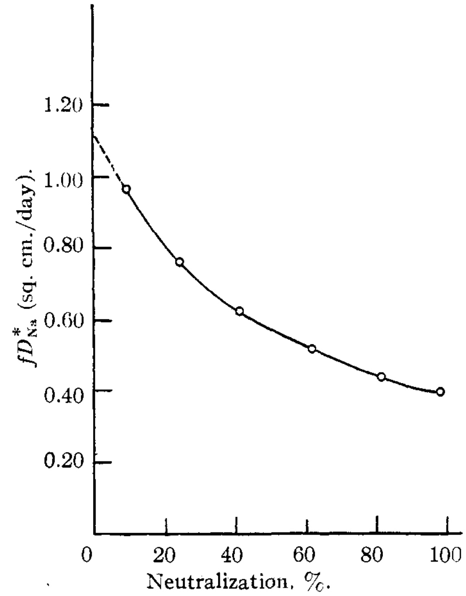

Fig. 2.—fD^*_{Na} as a function of neutralization for 0.0378 N polyacrylic acid.

In general the values of $1 - f$ as determined by diffusion and transference measurements are in satisfactory agreement, although the diffusion results are generally lower than the others. In view of the assumption that polymer ions have negligible mobilities, the diffusion values of $1 - f$ should be considered as lower limits. However, since f is directly proportional to ω_{Na} in equation (6) and shows a much weaker dependence on ω_{Na} in the transference case, some not unreason-

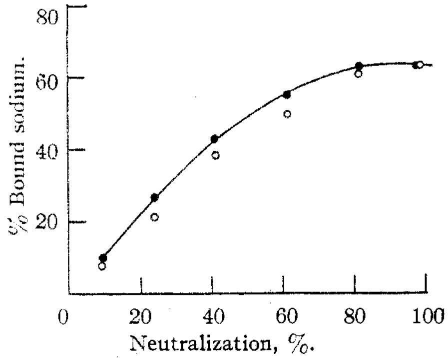

Fig. 3.—Sodium ion association as a function of neutralization for 0.0151 N polyacrylic acid: open circles, diffusion measurements; solid circles, transference measurements.[3]

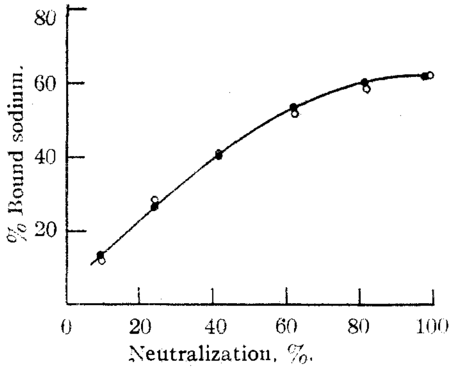

Fig. 4.—Sodium ion association as a function of neutralization for 0.0378 N polyacrylic acid: open circles, diffusion measurements; solid circles, transference measurements.[3]

able values of ω_{Na} can be chosen which will bring the two sets of results into even better agreement.

It was mentioned above that the values of f obtained from diffusion measurements do not depend on how the bound sodium is distributed among the different polymer species. The same is not true, however, for the transference calculation. If the polymer exhibits heterogeneity of mobilities, as might be expected, then the transference–conductance results will give rise to a different kind of average for f. Judging from the present results, the assumption of a narrow distribution of polymeric mobilities appears warranted.

At 61.7% neutralization the fraction of sodium ions associated with polymer is significantly lower at c = 0.00378 N than at 0.0151 N or 0.0378 N. Transference results show this quantity to be virtually constant over the higher concentration range 0.0151 N to 0.1189 N.

VI. Summary

1. The steady state diffusion of radioactive sodium ion in mixtures of polyacrylic acid and sodium hydroxide has been determined at 25°. Measurements have been made on the following solutions: stoichiometric polyacrylic acid concentration equal to 0.0151 and 0.0378 N, at 9.6, 24.0, 41.3, 61.7, 81.6, and 97.9% neutralization, and for an acid concentration equal to 0.00378 N at 61.7% neutralization.

2. Similar measurements were also made on four sodium chloride solutions in the range of concentration: 2×10^{-3} to 2×10^{-2} N. The results of these experiments were used to calibrate the diffusion cells.

3. For polyacrylic acid–sodium hydroxide solutions, extrapolation of the results to zero neutralization yields values of the mobility of sodium ion that are in good agreement with the known limiting mobility of sodium ion in pure water.

4. The fraction of sodium ions associated with polymer has been computed on the basis of the diffusion measurements. These results are in satisfactory agreement with those reported earlier based on transference measurements.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Absorption Spectra of Certain Nickel(II) and Cobalt(II) Complex Ions[1]

BY GRADY L. ROBERTS AND FRANK H. FIELD

In some recent work, Field and Vosburgh[2] found that certain magnetic properties of nickel(II) and cobalt(II) ions in the form of complex salts in aqueous solution were unexpectedly different. When the magnetic moments were calculated from the Curie equation, the formation of more stable complex ions resulted in a decrease in the nickel moment, but a small increase in the cobalt moment. The cobalt moments calculated from the Curie–Weiss equation decreased. It is of interest, therefore, to investigate more directly what changes occur in the energy levels of these ions as the stability of the complex ions changes.

We have measured the aqueous solution spectra of the cobalt(II) complex ions formed from water, oxalate ion, ammonia, ethylenediamine, and o-phenanthroline. In addition we have checked and extended previous work on the nickel(II) complex ions formed from these coördinating reagents.

All of these complex salts are known[2,3] to be para-

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(1) Taken from the M.A. thesis of G. L. Roberts, January, 1950.

(2) Field and Vosburgh, THIS JOURNAL, **71**, 2398 (1949).

(3) Russell, Cooper and Vosburgh, *ibid.*, **65**, 1301 (1943).